AN INVESTIGATION OF SOME TRIMETHYLPLATINUM COMPOUNDS

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
GLEN RICHARD HOFF
1967

ABSTRACT

AN INVESTIGATION OF SOME TRIMETHYLPLATINUM COMPOUNDS

by Glen Richard Hoff

Two forms of trimethylplatinum iodide have been reported in the literature: the more common tetrameric yellow form and the dimeric white form. As a dimeric structure would require unusual coordination for platinum(IV) or additional ligands, experiments were carried out the more clearly to identify the structure of the white form. The molecular weight of the white form has been determined more accurately than it had been previously and the earlier value is shown to be in error. Infrared spectra and x-ray powder diffraction patterns were also determined and are reported here. The molecular weights, infrared spectra, and x-ray powder diffraction patterns are the same for both forms, which indicates that they have the same tetrameric structure.

The infrared spectra, x-ray powder diffraction patterns, and equivalent conductance in aqueous solution of trimethylplatinum sulfate and nitrate were obtained and are reported. While the structures have not been determined, the results suggest that trimethylplatinum sulfate has four aquo groups and a bridging sulfate group and that trimethylplatinum nitrate has a unidentate nitrate group and two aquo groups.

AN INVESTIGATION OF SOME TRIMETHYLPLATINUM COMPOUNDS

By

Glen Richard Hoff

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1967

To Janet

ACKNOWLEDGMENT

The author wishes to express sincere appreciation to Professor Carl H. Brubaker, Jr. for his advice, guidance and encoragement throughout this project and to my wife, Janet, for her patience and understanding.

The author also wishes to thank the faculty, staff, and graduate students of the Department of Chemistry for the many helpful suggestions and advice.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION AND HISTORICAL BACKGROUND

There are a large number of sigma-bonded alkyl and aryl complexes of the transition metals[2-9,13] but most require that pi-bonding ligands, such as carbonyl groups or phosphine derivatives, also be present to lower the energy levels of the vacant d-orbitals and increase the stability of the metal organic compound[4]. However, platinum(IV) and gold(III) belong to a group of metals, including thallium(II), tin(IV), and lead(IV), whose alkyl derivatives do not need this stabilization and which give stable metal organic aquo cations[12,18,36].

The first of the platinum alkyl derivatives, yellow trimethylplatinum iodide, was prepared in 1909 by Pope and Peachey from the reaction of anhydrous platinum(IV) chloride with an excess of methylmagnesium iodide[39]. The yellow product was soluble in benzene and was shown by elemental analysis to have the formula C_3H_9PtI. By metathetical replacement of the iodine, Pope and Peachey obtained trimethylplatinum cyanide, chloride, and hydroxide, which were soluble in benzene, and sulfate and nitrate, which were soluble in water. They also prepared trimethyldiamminoiodoplatinum(IV) which has six ligands around the central atom as would be expected for normally octahedrally coordinated platinum(IV).

In 1933 Menzies and Overton found that molecular weight measurements indicated that the yellow form of

trimethylplatinum iodide, prepared by a method similar to that of Pope and Peachey, was tetrameric but the white form, prepared by adding potassium iodide to an aqueous solution of trimethylplatinum sulfate, was dimeric[34]. Rundle and Sturdivant, in 1947, determined the crystal structure of trimethylplatinum chloride and found it to be a tetramer with platinum atoms and chlorine atoms at alternate corners of a distorted cube[43]. The halogens are bridging so that each platinum atom is octahedrally coordinated.

In all reported cases platinum(IV) forms octahedral complexes. This is readily apparent in the case of derivatives such as trimethyldiamminoiodoplatinum and trimethylbis(pyridine)iodoplatinum but in some cases very unusual structures must be adopted. Trimethylplatinum chloride has three-way halogen bridges between platinum atoms. In acetylacetonate complexes of trimethylplatinum the acetylacetone may be mono-, bi- or tri-dentate; in the last case a dimer is formed in which the central carbon of acetylacetone occupies the sixth position around a platinum atom[14]. Cyclopentadiene occupies three positions of the octahedron in monomeric cyclopentadienyltrimethylplatinum[40]. All other reported trimethylplatinum compounds have octahedrally coordinated platinum and the three methyl groups are always cis to one another[12,43].

It is possible to prepare many derivatives of trimethylplatinum by exchange of the non-methyl ligands[16,25,29]. However, in all reported cases there is no migration of the

methyl groups from positions cis to one another and it is not possible to remove any of the methyl groups without immediate decomposition of the compound.

In most cases of sigma-bonded metal organic compounds the stability of the metal aryls is greater than that of the metal alkyls. However, attempts to prepare platinum(IV) aryls have been unsuccessful because there is a greater steric hindrance between the aryls than there is between the alkyls in the tetrameric structure of the organoplatinum compound[13]. The only alkylplatinum(IV) compounds which have been synthesized have been those containing either three methyl or three ethyl groups. Triethylplatinum iodide was first prepared by S. F. A. Kettle by the reaction of diethylmercury with anhydrous platinum tetrachloride[26].

In 1952 Gilman, Lichtenwalter, and Benkeser carefully studied the reaction used by Pope and Peachey to prepare trimethylplatinum iodide and reported that in addition to the major product, small amounts of tetramethylplatinum, dimethylplatinum diiodide, methylplatinum(VI) pentaiodide, and several unidentified organoplatinum compounds were also formed[20]. The synthesis of these compounds has not been successfully repeated but it seems unlikely that a platinum(VI) compound would be obtained from platinum(IV) in the reducing medium of a Grignard reagent[13]. Tetramethylplatinum had been previously prepared by Lichtenwalter in 1938 by the reaction of trimethylplatinum iodide with methylsodium[19]. He also prepared hexamethyldiplatinum by reacting

trimethylplatinum iodide with powdered potassium. Rundle and Sturdivant determined that tetramethylplatinum was tetrameric and isostructural with trimethylplatinum chloride and that hexamethyldiplatinum crystallized in polymeric chains[13,43].

Attempts to duplicate the synthesis of tetramethylplatinum have not been successful. Hoechstetter repeated the preparation according to the description given by Lichtenwalter and found that the products were white trimethylplatinum iodide, trimethylplatinum hydroxide, and trimethylplatinum methoxide[23]. Modifications and improvements in the synthetic technique gave either the starting material or a mixture of trimethylplatinum methoxide and trimethylplatinum hydroxide. In light of the evidence, Hoechstetter compared the available spectral data and found that the X-ray powder diffraction patterns of trimethylplatinum hydroxide and that reported for tetramethylplatinum were very similar in "d"-spacings and intensities. It would appear from the evidence presented by Hoechstetter and others that tetramethylplatinum and hexamethyldiplatinum have not yet been synthesized.

Trimethylplatinum derivatives have only been partially characterized. Infrared spectral data are avilable for mixed derivatives with halogens, ammonia, pyridine, and several other ligands[21,24,31,40]. The structures of several trimethylplatinum acetylacetonates and related ligands have been determined[29,41,46]. Kite, Smith, and Wilkins examined the nuclear magnetic resonance spectra and structures of twenty-three trimethylplatinum compounds and demonstrated

that the spin-spin coupling constant between methyl protons and ^{195}Pt is sensitive to the chemical nature of the non-methyl ligands[28]. Raman spectra of trimethylplatinum sulfate, nitrate, and perchlorate show that these compounds are extensively dissociated in aqueous solution[11]. Other than nuclear magnetic resonance data, no further studies on these ionic trimethylplatinum derivatives have been reported.

EXPERIMENTAL

Materials

Platinum.- Scrap wire and sheet platinum were obtained from departmental stores and cleaned by boiling in 37% hydrochloric acid.

Methyl Iodide.- Reagent grade methyl iodide was refluxed and distilled from anhydrous calcium chloride immediately before use.

Ether.- Anhydrous diethyl ether was obtained by refluxing reagent grade anhydrous ether with lithium aluminum hydride for twenty-four hours and distilling immediately before use.

Benzene.- Benzene, used for the determination of molecular weights, was obtained by twice distilling reagent-grade, thiophene-free benzene from sodium and collecting the fraction which distilled at $80.1^0 \pm 0.1^0$ (uncorrected). Benzene for other purposes was reagent grade and was freshly distilled once from sodium.

Chloroform.- Reagent grade chloroform was used without further purification.

Potassium Chloride.- Potassium chloride used for the calibration of the conductance cell had been previously purified by the method of Scathard, Hamer and Wood[44] in which reagent grade potassium chloride was dissolved in conductance water

and precipitated by hydrogen chloride gas. The powder thus obtained was dried at 300° and then at room temperature by passing through it a stream of air dried by calcium chloride. Immediately before use it was dried at 110° for several days.

Potassium Bromide.- Finely divided potassium bromide for infrared spectroscopy was dried at 110° for several days.

Other Materials.- Other materials used in this study were reagent grade and used without further purification.

Methods of Elemental Analysis

Platinum.- A weighed quantity of sample in a porcelain crucible was wetted with chloroform and sulfuric acid (1:4) and a few crystals of iodine were added. The sample was carefully heated in a muffle furnace at 100° until decomposition was complete and then the temperature was slowly increased to 900° and held there five hours. The metallic residue was weighed as platinum.

Iodine.- Iodine was determined by fusion of a sample with sodium bicarbonate, carefully dissolving the cake in dilute nitric acid, and titrating the acid solution for iodine by adding silver nitrate to precipitate silver iodide and titrating the excess silver nitrate with potassium thiocyanate.

Sulfate.- Sulfate was determined gravimetrically as barium sulfate by adding barium nitrate to an aqueous solution of

the sample in a fine porosity porcelain filter crucible, carefully washing the precipitate to remove coprecipitated nitrates, and igniting the precipitate at 900°.

Methods of Analytical Analysis

Infrared Analysis.- Infrared analysis in the 650-5000 cm^{-1} region were obtained with a Unicam SP-200 spectrophotometer with sodium chloride optics. Samples were run in potassium bromide pellets and mulls of Nujol, Fluorolube, and 1,3-hexachlorobutadiene. Analysis in the 200-650 cm^{-1} region were obtained with a Beckman IR-7 spectrophotometer with cesium iodide optics. Nujol mulls of the sample were mounted in polyethylene plates.

X-ray Powder Diffraction.- The X-ray powder diffraction patterns were made by the Debye-Scherrer method with a Phillips 114.59 mm diameter camera. The source of radiation was a copper target (20ma; 40 kv) with a nickel filter which provides a K_α x-ray of 1.5418 Å (unresolved). Samples were run in 0.3 mm glass capillaries for twenty hours.

Molecular Weights.- The molecular weights were determined with a Mechrolab vapor pressure osmometer with a non-aqueous probe designed to operate at 37°. The solvent employed was benzene and the vapor pressure osmometer was calibrated with benzil.

Conductance Measurements.- A Wayne Kerr Universal Bridge B221 was used with a modified Shedlovsky cell. Trimethylplatinum sulfate was studied by adding a series of weighed portions of the solid to a known volume of water already in the cell. Trimethylplatinum nitrate was analyzed by preparing an aqueous solution of the nitrate directly from the sulfate, diluting it to a known volume, and making subsequent dilutions to complete the study.

Preparation of the Compounds

Potassium Hexachloroplatinate(IV).

Scrap platinum was dissolved in aqua regia and after reduction of the volume to 25 ml by evaporation, hydrochloric acid was added and the volume again reduced. This latter step was repeated until all of the nitrogen oxides had been removed. Potassium chloride was added to the solution and potassium hexachloroplatinate(IV) was collected on a Büchner filter as a yellow powder, washed with dilute hydrochloric acid and water, and dried at 110^0.

Trimethylplatinum Iodide (yellow form).

The yellow form of trimethylplatinum iodide was prepared according to the directions of Clegg and Hall[11]. The Grignard reagent methylmagnesium iodide was prepared by the slow addition of 14.5 ml (0.23 mole) of methyl iodide to 3.5 g (0.14 mole) of magnesium in 100 ml of ether, during which the mixture was cooled in an ice bath and stirred continually. The mixture was refluxed twenty minutes, again cooled in an ice bath, and the Grignard reagent decanted into a dropping funnel. The use of excess Grignard reagent in the subsequent preparation of trimethylplatinum iodide increases the yield. It has been reported that the excess methyl iodide oxidizes platinum(II) compounds which are formed by the reduction of platinum(IV) by methylmagnesium iodide[1].

Ten grams (0.02 mole) of potassium hexachloroplatinate(IV) was added to a mixture of 100 ml of benzene and 50 ml of ether previously distilled into a 500 ml three-neck flask which was fitted with a stirrer, a reflux condenser, and the dropping funnel containing the methylmagnesium iodide. Nitrogen was swept over the mixture which was also protected with a calcium chloride guard tube. The mixture was cooled in an ice bath and the Grignard reagent was slowly added over a ten minute period while the solution was stirred continually. The ice bath was then removed and stirring was continued for several hours. The mixture then stood at ambient temperature for twenty hours during which an off-white solid settled and the solvent layer became clear and faintly orange-colored. On the basis of several preparations by the technique of Clegg and Hall, it is recommended that the stirring after removal of the ice bath be continued for three hours after the mixture lightens to a very pale yellow or off-white, which first occurs from four to six hours after the addition of the Grignard reagent.

The mixture was cooled in an ice bath and an ice slurry of 100 ml of 10% hydrochloric acid was slowly added with stirring. The organic layer became orange and the aqueous layer became a very deep orange. The organic layer was decanted and 100 ml of benzene were added to the aqueous layer. The mixture was refluxed and stirred for twenty minutes and the benzene layer was decanted. This step was repeated twice and the combined extracts and original organic

layer were placed over anhydrous sodium sulfate. After twenty hours the mixture was filtered and the clear filtrate was evaporated to dryness in a stream of air. The residue was washed by decantation once with five milliliters of ethanol to remove the dark-colored material and then dissolved in hot chloroform. The chloroform was evaporated in an air stream to half the volume of solution present when the first crystals appeared, and an equal volume of acetone was added. After the mixture was cooled and filtered, the yellow-brown powder collected on the filter was recrystallized from a chloroform-acetone mixture and dried at 110^0. Yields were 75-85%, higher than those reported by Clegg and Hall. Analysis. Calculated for C_3H_9PtI: Pt, 53.14%; I, 34.06%. Found: Pt, 53.06%; I, 33.4%.

Trimethylplatinum iodide is soluble in benzene, chloroform, dimethylsulfoxide, tetrahydrofuran, and dimethylformamide. It is insoluble in water, acetone, methanol, and ethanol. The color of the original product may be lightened slightly by dissolving the powder in the minimum amount of hot chloroform, evaporating the solution to half the original volume, and adding to it an equal volume of acetone. The powder obtained after cooling and filtering is finely divided and bright yellow. Evaporation of the filtrate and wash solutions gives a coarse powder darker than the original starting material.

A very light yellow or beige form of trimethylplatinum iodide was obtained by refluxing a chloroform solution of

dark yellow trimethylplatinum iodide with silver sulfate. After the mixture had refluxed several hours, during which the initial yellow color became lighter, it was filtered to remove the green powder containing largely silver salts and the volume of the filtrate was reduced by evaporation in a stream of air to half the volume present when crystals first appeared. An equal volume of acetone was added, the mixture was cooled, and the light yellow trimethylplatinum iodide powder was collected on a Büchner filter, washed with acetone, and dried at 110°. A white form of trimethylplatinum iodide has not been prepared by this method.

When dark yellow trimethylplatinum iodide was dissolved in chloroform or benzene a small quantity of a dark powder appeared after a short time. The solid was insoluble in hot chloroform and gave an orange-brown smear on filter paper. Analysis. Calculated for PtI_2: Pt, 43.4%. Found: Pt, 44.8%. It was also observed that dry yellow trimethylplatinum darkened with age and exposure to light but that the color could be lightened by recrystallization or refluxing the solid with silver sulfate in chloroform.

Trimethylplatinum Sulfate.

Trimethylplatinum sulfate was prepared by the reaction between silver sulfate and trimethylplatinum iodide[39,25]. Trimethylplatinum iodide (4.73 g, 0.013 mole) was dissolved in 100 ml of hot benzene and 2.5 g (0.008 mole) of silver sulfate and 100 ml of moist acetone were added. The mixture

was refluxed with stirring for about eight hours until the initially yellow solution had turned colorless. The mixture was filtered to remove the silver salts and the filtrate was evaporated to partial dryness in an air stream. The water in the moist acetone prevented complete drying in the stream of air. The partially dry solid was dissolved in acetone and a black powder was removed by filtration. The solvent was evaporated to half the original volume when crystals first reappeared and an equal volume of chloroform was added. The finely divided crystals were collected on a filter and washed with chloroform. The crystals of trimethylplatinum sulfate were then recrystallized from water and dried at room temperature in a vacuum desiccator with phosphorus pentoxide. The yield was 0.84 g (85%) of white feathery plates of trimethylplatinum sulfate $[(CH_3)_3Pt]_2SO_4 \cdot 4\ H_2O$. Analysis. Calculated: Pt, 60.54%; SO_4, 14.91%. Found: Pt, 60.29%; SO_4, 15.04%.

Trimethylplatinum sulfate is soluble in water and acetone and insoluble in benzene and chloroform. The compound decomposes before the waters of crystallization can be driven off by heating. The dry compound was heated to 110^0 without decomposition but partially dry compounds decomposed to platinum and unidentified residues at temperatures as low as 40^0. It is difficult to purify completely the trimethylplatinum sulfate by crystallization owing to its ready solubility, so impurities may color the product cream or light brown. Acetone-chloroform filtrates from recrystallization

and other solutions of trimethylplatinum sulfate which had partially decomposed were green and contained a small quantity of black powder. If the powder was removed by filtration, more appeared in the filtrate and crystalline trimethylplatinum sulfate could not be obtained free of green or black discoloration.

Trimethylplatinum Nitrate.

Trimethylplatinum nitrate was prepared by the metathetical reaction between barium nitrate and trimethylplatinum sulfate in an aqueous solution[25,39]. After the barium sulfate was removed by filtration, the fitrate was evaporated to partial dryness in an air stream and drying was completed in a vacuum desiccator with phosphorous pentoxide. The cream colored crystals, reported to be $(CH_3)_3PtNO_3 \cdot 2\ H_2O$, could not be further purified to remove the color. Trimethylplatinum nitrate is soluble in water and acetone and insoluble in benzene and chloroform. The crystals were very deliquescent so an elemental analysis was not obtained for trimethylplatinum nitrate.

Trimethylplatinum Iodide (white form).

The white form of trimethylplatinum iodide was easily obtained by adding potassium iodide to an aqueous solution of trimethylplatinum sulfate or trimethylplatinum nitrate. A white precipitate immediately formed and was collected on a filter after the mixture had been cooled in an ice

bath for ten minutes. The white packed powder was washed with cold water and dried at 110°. Analysis. Calculated for C_3H_9PtI: Pt, 53.14%; I, 34.06%. Found: Pt, 54.10%; I, 34.0%.

White trimethylplatinum iodide is similar to the yellow form in properties except for the difference in color. The white form is converted to the yellow form readily in chloroform but in benzene it is converted slowly and with heating. A solution of white trimethylplatinum iodide in benzene did not give the dark solid found in similar solutions of the yellow form.

If precipitated trimethylplatinum iodide is not removed from the original aqueous solution, oxidation of excess iodide ion in the solution colors the solid a faint brown. A similarly colored product is obtained if white trimethylplatinum iodide is precipitated from a solution containing iodine as I_3^-. Most of the color is removed by washing the solid with water and drying it at 110°.

RESULTS AND DISCUSSION

Trimethylplatinum chloride and yellow trimethylplatinum iodide are tetrameric, but white trimethylplatinum iodide is reported to be dimeric. A dimeric structure for trimethylplatinum iodide would require that either the platinum(IV) atom not be octahedrally coordinated or that additional ligands be present. Since no data other than the molecular weight and elemental analysis have been published for the white compound, one objective of the present investigation was to compare the two forms of trimethylplatinum iodide and identify the structure of the white form.

The experimental infrared spectrum of yellow trimethylplatinum iodide (Table 1) is similar to that reported by Hoechstetter[24] and Gribov et al.[21] and spectral assignments are made accordingly. There are no observable differences in the spectra for the white and yellow form of trimethylplatinum iodide.

There is a close correlation between the x-ray powder diffraction patterns (Table 2) for the two forms of trimethylplatinum iodide although there are a few anomalies. The number of lines and the absence of regular spacing shows that trimethylplatinum iodide does not have the body-centered cubic structure of trimethylplatinum chloride and that the structure cannot be determined from the powder pattern alone.

Table 1. Infrared spectrum of trimethylplatinum iodide[a]

Experimental (cm^{-1})	Literature[21,24]	Assignment
554 w	562 vw	Pt-C stretch
862 vw	852 vw	Pt-C bending
---	882 w	Methyl rocking
1218 s	1218 s	Symmetric C-H deformation
1257 s	1253 s	Degenerate (methyl rocking) C-H deformation
1410 m	1406 m	Unsymmetric (degenerate) C-H deformation
2770 w	2775 w	Overtone from unsymmetric C-H deformation
2870 m	2874 m	Symmetric C-H stretch
2940 m	2950 m	Unsymmetric (degenerate) C-H stretch

[a]s, strong; m, medium; w, weak; vw, very weak.

Table 2. "d"-spacings for trimethylplatinum iodide[a]

Yellow Form	White Form
8.59 m	8.60 w
8.13 s	8.15 s
7.74 m	7.75 m
7.24 m	7.26 m
6.32 s	6.30 s
5.06 w	5.07 w
4.61 w	4.64 w
4.36 w	4.34 w
----	4.04 vw
3.79 vw	3.79 vw
3.67 vw	----
3.43 vw	3.47 vw
3.33 vw	3.34 vw
3.22 w	3.23 s
3.14 s	3.15 m
3.03 m	3.05 m
2.98 m	----
2.91 m	2.91 s
2.83 m	2.82 s
2.69 vw	----
2.62 w	2.62 w
2.57 vw	2.57 vw
2.54 vw	----
2.49 vw	2.49 s
2.41 s	2.41 m
2.38 vw	----
2.36 vw	2.36 m
2.30 w	2.30 vw
2.22 w	2.22 w
2.20 w	2.19 m
2.16 w	----
2.11 w	2.10 w
2.05 m	2.06 w
2.03 vw	2.03 vw
1.98 m	1.97 m
1.89 vw	1.90 w
1.88 vw	----
1.87 vw	1.86 w
1.84 vw	----
1.78 vw	1.76 vw
----	1.73 vw
----	1.71 vw
----	1.65 vw
1.62 vw	1.62 vw
1.60 vw	1.60 vw
	1.58 vw
Other very faint lines	1.55 vw

[a]s, strong; m, medium; w, weak; v, very; b, broad.

Foss and Gibson[16] determined the molecular weights of both forms of trimethylplatinum iodide by ebullioscopic and Barger's method and reported association factors of 3.20-3.40 for the yellow compound and 2.42 for the white compound. A redetermination of the molecular weights by the author indicates that both forms of trimethylplatinum iodide are tetrameric in solution. The association factors are 4.01 for the yellow form and 4.07 for the white form. As the white form, in a benzene solution, is converted to the yellow with time and heat, the data collected by vapor pressure osmometry should be more accurate than that of the more time consuming methods used by Foss and Gibson.

The results of these experiments indicate that the white and yellow forms of trimethylplatinum iodide have identical structures and differ only in color. Octahedral coordination has been found in all reported structures of platinum(IV) compounds and the present investigation has uncovered no evidence for the presence of additional ligands. The color of the yellow compound is believed to be caused by adsorbed iodine since most of it may be removed when the compound is refluxed with a silver salt and the white compound is obtained when methylsodium is used in the synthesis instead of methylmagnesium iodide.[24]

Trimethylplatinum sulfate and nitrate are of interest because of their ionic character as compared to the highly covalent character of most of the trimethylplatinum derivatives. Raman spectroscopy was used by Clegg and Hall[12] to

show the extensive dissociation of these compounds in aqueous solution. An objective of the present study was to determine the structures of the solid compounds and find if, in trimethylplatinum sulfate, two trimethylplatinum groups are joined together.

The presence of three sulfate sulfate peaks in the 900-1200 cm^{-1} region of the infrared spectrum of trimethylplatinum sulfate (Table 3) shows that in the crystalline state the sulfate group has a C_{2v} symmetry which indicates that it is bridging or bidentate.[38] Water is present but it could not be determined from the spectrum whether it is coordinated or lattice water. Resolution in the far infrared region has not been great enough to provide any additional information about the structure of the molecule. With potassium bromide pellets a shift in the spectrum of the C-H frequencies and the appearance of a peak corresponding to ionic sulfate indicates that trimethylplatinum bromide is formed when the pellet is prepared.

Two different spectra are obtained for trimethylplatinum nitrate (Table 4) depending upon the technique used. The spectrum of the sample in a potassium bromide pellet corresponds to that of trimethylplatinum bromide and free nitrate ion although the correlation with the published values for the nitrate group[38] is not good and some of the peaks may be caused by impurities. A Nujol (mineral oil) mull of the solid gives a similar spectrum but with several additional peaks which are attributed to a coordinated

Table 3. Infrared spectrum of trimethylplatinum sulfate.

Experimental (cm^{-1})	Literature[24,38]	Assignment
554 m	562 vw	Pt-C stretch
985 m	995 m	Sulfate (ν_1)
1080 s	1050-1060 s	Sulfate (ν_3)
1110 s	1105 s	Sulfate (ν_3)
1160 s	1170 s	Sulfate (ν_3)
1240 s	1218 s	Comb. Sym. C-H deformation
	1253 s	Deg. C-H deformation
1410 m	1406 m	Unsym. C-H bending
1630 s	1630-1600 s	Water
2150 w	2150 m	Sulfate
2790 w	2775 w	Overtone unsym. C-H bending
2890 m	2874 m	Sym. C-H stretch
2960 m	2950 m	Unsym. C-H stretch
3370 s 3450 s	3200-3550 s	Water

Table 1. Infrared spectrum of trimethylplatinum nitrate.

KBr	Nujol	Literature	Assignment
---	720 w	721 vs	Pt-O stretch (water)
732 m	730 m	700-800	Nitrate (ν_4)
822 m	812 w	815-830	Nitrate (ν_2)
832 m	822 m		
885 m	897 m	882	Methyl rock
---	1040 s	970-1035	Nitrate (coordinated) (ν_1)
1225 s	1230 w	1218	C-H deformation
1247 w	1235 s		
1265 m	1285 m	1253	C-H deformation
---	1320 m		Nitrate (coordinated) (ν_3)
1385 m	1360 s	a	Nitrate
1410 w	1410 vw	1406	C-H deformation
1420 w	1420 m	a	Nitrate
1637 m	1635 m	1600-1635	Water
1755 w	1755 w	a	Nitrate
1770 m	1772 m	a	Nitrate
2350 w	1340 w		
2450 m	2450 m		
2780 w	2780 w	2770	C-H deformation
2880 m	2880 m	2874	C-H stretch
2950 m	2930 m	2930	C-H stretch
3350 s	3380 s	3200-3550	Water
	3450 s		

[a]Not reported in literature, but assumed to be caused by nitrate as it only appears in the spectra of trimethylplatinum nitrate.

nitrate group. When hexachlorobutadiene is used as the mulling agent the spectrum initially shows the presence of the coordinated nitrate group, but over a short period of time a reaction takes place and the spectrum changes to one resembling a trimethylplatinum halide. Infrared spectra alone are not sufficient to establish whether the nitrate is unidentate or bidentate.

The x-ray powder diffraction patterns of trimethylplatinum sulfate and nitrate are given in Tables 5 and 6. There is no similarity between the patterns for the iodide, nitrate, or sulfate. The structures cannot be determined from the powder patterns because of the large number of lines and single crystals could not be grown.

Trimethylplatinum sulfate and nitrate readily dissolve in water and the shapes of the equivalent conductance curves (Figures 1 and 2) show that they are strong electrolytes. A comparison of graphs of experimental data with theoretical Onsager graphs indicates that trimethylplatinum sulfate is a 2:1 electroltye and trimethylplatinum nitrate is a 1:1 electrolyte.

While the structure of trimethylplatinum sulfate has not been determined, the experimental results suggest that the sulfate group bridges two platinum atoms. The bridge is readily broken and the sulfate group replaced by other anions. The remaining two positions in the coordination sphere of each platinum atom are probably occupied by aquo groups. The probable structure of trimethylplatinum nitrate

Table 5. "d"-spacings for trimethylplatinum sulfate

11.30 s	2.20 w
10.40 s	2.15 s
6.41 vw	2.08 vw
6.17 m	2.03 w
5.55 vs	1.99 w
5.27 vs	1.96 m
5.05 s	1.90 vw
4.91 s	1.87 w
4.45 m	1.80 w
4.18 w	1.73 m
3.38 vw	1.66 vw
3.58 vw	1.62 w
3.42 vw	1.60 w
3.38 m	1.58 w
3.26 m	1.56 w
3.05 s (b)	1.54 w
2.84 vw	1.50 w
2.73 m	1.48 vw
2.68 s	1.43 w (b)
2.53 vw	1.40 vw
2.47 m	1.38 vw
2.43 m	1.35 w
2.40 vw	1.34 w
2.35 w	1.30 w (b)
2.29 w	1.25 vw

Table 6. "d"-spacings for trimethylplatinum nitrate

5.91 m	2.15 w
5.72 s	2.07 vvw
5.26 s	2.02 m
4.64 s	1.98 w
4.03 m	1.93 w
3.81 w	1.86 m
3.61 w	1.83 m
3.30 w	1.81 m
3.23 w	1.65 m
3.17 w	1.59 vw
2.95 vw	1.56 m
2.90 vw	1.52 vw
2.85 w	1.47 vvw
2.78 vw	1.45 vw
2.74 w	1.43 vw
2.70 vw	1.37 s
2.51 vw	1.35 m
2.47 vw	1.28 w
2.44 s	1.24 m
2.34 m	1.14 w
2.30 w	1.04 w
2.20 w	

Figure 1. Equivalent conductance of trimethylplatinum sulfate in aqueous solution.

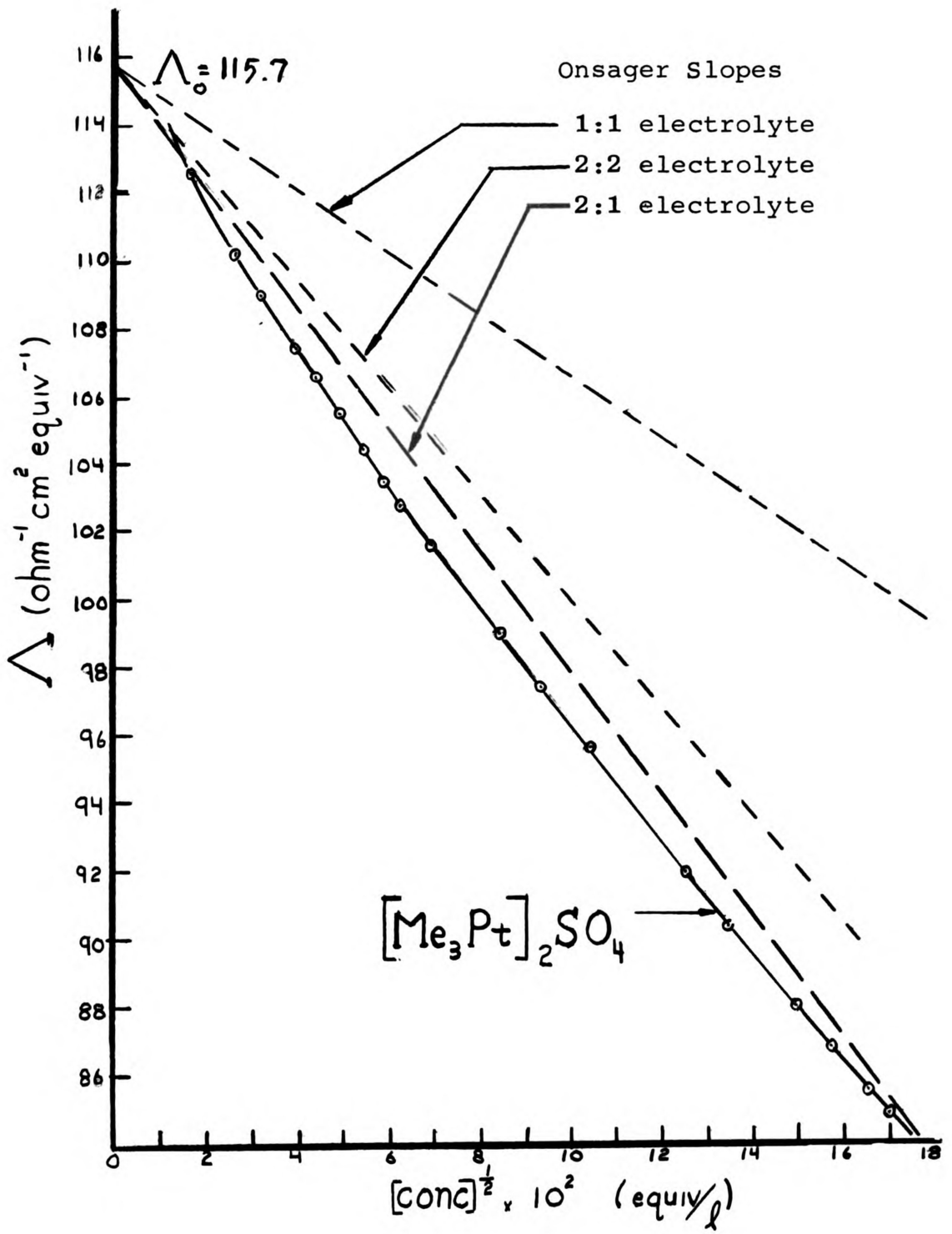
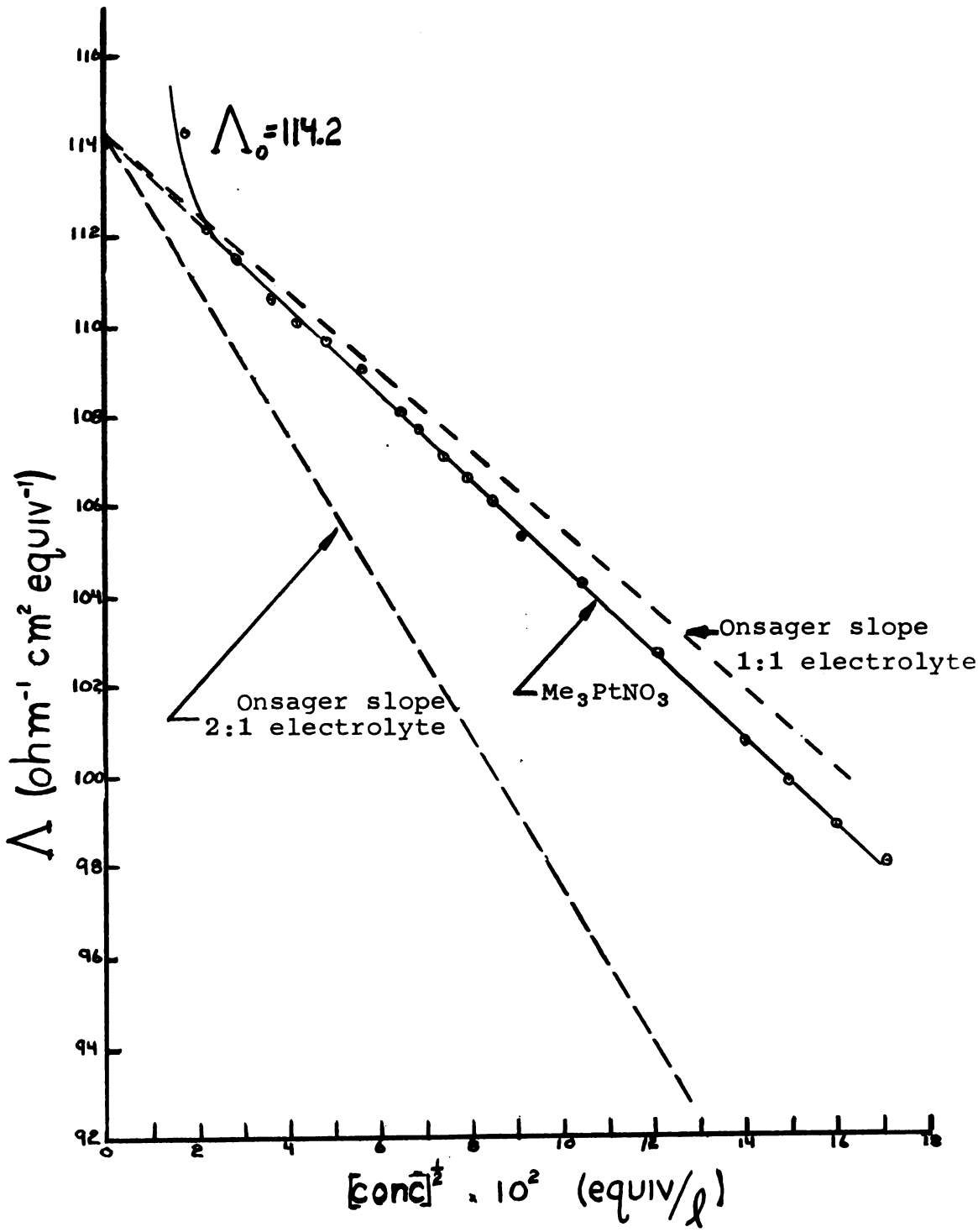


Figure 2. Equivalent conductance of trimethylplatinum nitrate in aqueous solution



is a unidentate nitrate group and two aquo groups occupying the three non-methyl ligand positions.

SUMMARY

Trimethylplatinum derivatives are of interest because of their high degree of stability and the non-mobility of the methyl ligands. Many trimethylplatinum compounds have been prepared but only limited characterization has been achieved for most of them. The purpose of the present investigation was to characterize the white trimethylplatinum iodide, trimethylplatinum sulfate and trimethylplatinum nitrate.

The white form of trimethylplatinum iodide has been reported to be dimeric, in contrast to the more common yellow form which is tetrameric. A dimeric structure would require that either additional ligands be present or an unusual coordination for platinum(IV). Only the molecular weights and elemental analysis of both forms of trimethylplatinum iodide and the infrared spectrum of the yellow form have been reported in the literature. For a comparison of the two structures, the previously reported analysis and spectrum were confirmed and the infrared spectrum of the white form and x-ray powder diffraction patterns of both forms were determined. Molecular weight measurements, more accurate than those which had been reported previously, indicate that both forms are tetrameric in solution. The infrared spectrum and x-ray patterns are the same for both white and yellow trimethylplatinum iodide which indicates that they have the same tetrameric structure.

No structural information has been reported for the ionic compounds trimethylplatinum sulfate and nitrate except elemental analysis. In the present study, the infrared spectra, x-ray powder diffraction patterns, and equivalent conductance in aqueous solution were determined. In aqueous solution, both trimethylplatinum sulfate and nitrate are strongly dissociated. Trimethylplatinum sulfate is a 2:1 electrolyte and trimethylplatinum nitrate is a 1:1 electrolyte. The structures of both compounds cannot be determined from the diffraction patterns because of the large number of lines, but the infrared spectra and elemental analysis indicate that trimethylplatinum sulfate has a sulfate group bridging two platinum atoms and two aquo groups on each of the platinum atoms and that trimethylplatinum nitrate has two aquo groups and an unidentate nitrate group attached to the platinum atom.

BIBLIOGRAPHY

1. Adams, D. M., Chatt, J., and Shaw, B. L., J. Chem. Soc., 2047 (1960).

2. Chatt, J., Garforth, J. D., and Rowe, G. A., J. Chem. Soc., 1834 (1966).

3. Chatt, J., and Hayter, R. G., J. Chem. Soc., 6017 (1963).

4. Chatt, J., and Shaw, B. L., J. Chem. Soc., 705 (1959).

5. Chatt, J., and Shaw, B. L., J. Chem. Soc., 4021 (1959).

6. Chatt, J., and Shaw, B. L., J. Chem. Soc., 1718 (1960).

7. Chatt, J., and Shaw, B. L., J. Chem. Soc., 285 (1961).

8. Chatt, J., and Shaw, B. L., J. Chem. Soc., 1836 (1966).

9. Chatt, J., and Underhill, A. E., J. Chem. Soc., 2089 (1963).

10. Chatterjee, A. K., Menzies, R. C., Steel, J. R., and Youdale, R. N., J. Chem. Soc., 1707 (1958).

11. Clegg, D. E., and Hall, J. R., Inorganic Syntheses, to be published.

12. Clegg, D. E., and Hall, J. R., Spectrochim. Acta, 21: 357 (1965).

13. Cotton, F. A., Chem. Rev., 55:551 (1955).

14. Cotton, F. A., and Wilkinson, G., Advanced Inorganic Chemistry. 2d ed. revised. New York: Interscience Publishers, 1966.

15. Cox, E. G., and Webster, K. C., Z. Krist., 90:561 (1935).

16. Foss, M. E., and Gibson, C. S., J. Chem. Soc., 299 (1951).

17. Fritz, H. P., and Schwarzhans, K-E., J. Organomet. Chem., 5:181 (1966).

18. Gibson, C. S., and Weller, W. T., J. Chem. Soc., 103 (1941).

19. Gilman, H., and Lichtenwalter, M., J. Amer. Chem. Soc. 60:3085 (1938).

20. Gilman, H., Lichtenwalter, M., and Benkeser, R. A., J. Amer. Chem. Soc., 75:2063 (1953).

21. Gribov, L. A., Gel'man, A. D., Zakarova, F. A., and Orlova, M. M., Zh. Neorg. Khim., 5:987 (1960).

22. Hall, J. R., Private communication.

23. Hoechstetter, M. N., Ph.D. Thesis, Michigan State University (1960).

24. Hoechstetter, M. N., J. Mol. Spect., 13:407 (1964).

25. Invanova, O. M., and Gel'man, A. D., Zh. Neorg. Khim., 3:1334 (1958).

26. Kettle, S. F. A., J. Chem. Soc., 5737 (1965).

27. Kettle, S. F. A., J. Chem. Soc., 5737 (1965).

28. Kite, K., Smith, J. A. S., and Wilkins, E. J., J. Chem. Soc., 1744 (1966).

29. Kite, K. and Truter, M. R., J. Chem. Soc., 207 (1966).

30. Lewis, J., Long, R. F., and Oldham, C., J. Chem. Soc., 6740 (1965).

31. Lile, W. J., and Menzies, R. C., J. Chem. Soc., 1169 (1949).

32. Lyndon, J. E., and Truter, M. R., J. Chem. Soc., 6899 (1965).

33. Lyndon, J. E., Truter, M. R., and Watling, R. C., Proc. Roy. Soc., 193 (1964).

34. Menzies, R. C., and Overton, H., J. Chem. Soc., 1290 (1933).

35. Menzies, R. C., and Wiltshire, E. R., J. Chem. Soc., 21 (1933).

36. Miles, M. G., Glass, G. E., and Tobias, R. S., J. Amer. Chem. Soc., 88:5738 (1966).

37. Morgan, G. L., Rennick, R. D., Soong, C. E., Inorg. Chem., 5:372 (1966).

38. Nakamoto, K., Infrared Spectra of Inorganic and Coordination Compounds. New York: John Wiley and Sons Inc., 1963.

39. Pope, W. J., and Peachey, S. J., J. Chem. Soc., 95:571 (1909).

40. Robinson, S. D., and Shaw, B. L., Z. Naturforsch., 18b:507 (1963).

41. Robson, A., and Truter, M. R., J. Chem. Soc., 630 (1965).

42. Rundle, R. E., and Holman, E. J., J. Amer. Chem. Soc., 69:1561 (1947).

43. Rundle, R. E., and Sturfivant, J. H., J. Amer. Chem. Soc., 69:1561 (1947).

44. Satchard, G., Hamer, W. J., and Wood, S. E., J. Amer. Chem. Soc., 60:3061 (1938).

45. Smith, J. A. S., J. Chem. Soc., 4736 (1965).

46. Truter, M. R., and Cox, E. G., J. Chem. Soc., 948 (1956).